

POTENTIAL USE OF GRAFT COPOLYMERS OF MERCERIZED FLAX AS FILLER IN POLYSTYRENE COMPOSITE MATERIALS

Susheel Kalia,^{1*} Sanjeev Sharma,¹ Bandna Bhardwaj,¹ B.S. Kaith,² and A.S. Singha³

Graft copolymerization of binary vinyl monomers onto mercerized flax fiber was carried out for the enhancement of mechanical properties of polystyrene composites. Binary vinyl monomer mixture of AA+AN has been found to show maximum grafting (33.55%) onto mercerized flax. Graft copolymers thus synthesized were characterized with FT-IR spectroscopy, SEM, and TGA techniques. Mercerized flax (MF) showed maximum thermal stability in comparison to graft copolymers. It has been found that polystyrene composites reinforced with graft copolymers showed improvement in mechanical properties such as wear resistance, compressive strength, and tensile strength.

Keywords: Fiber Modification; Composites; Mechanical Properties

*Contact information: 1: Department of Chemistry, Singhania University, Pacheri Bari, Jhunjhunu – 333 515 (Rajasthan) India; 2: Department of Chemistry, Dr. B.R. Ambedkar National Institute of Technology (Deemed University), Jalandhar - 144 011 (Pb.) India; 3: Department of Applied Sciences, National Institute of Technology (Deemed University), Hamirpur – 177 005 (H.P.) India; *Corresponding author: susheel_kalia@yahoo.com, susheel.kalia@gmail.com*

INTRODUCTION

Flax fiber is a favorable reinforcing material for composites due to ecological and environmental merits and attractive mechanical properties. Flax fiber is considered to be one of the strongest fibers among the natural fibers. Moisture causes degradation of mechanical properties of composites reinforced with natural fibers to a larger extent in comparison to composites reinforced with synthetic fibers, as a consequence of the higher moisture sorption behaviour and the organic nature of natural fibers (Karmaker 1997; Katz et al. 1987). In order to develop composites with better mechanical properties and environmental performance, it becomes necessary to increase the hydrophobicity of the natural fibers and to improve the interface between the matrix and natural fibers. Graft copolymerization of natural fibers is one of the best methods to attain these improvements. Graft copolymerization of vinyl monomers onto cellulose has been reported by various authors (Kaith and Kalia 2007, 2008, 2008; Kaith et al. 2005; Nada et al. 2007). Only few workers have reported the use of graft copolymers of natural fibers as reinforcing material in the preparation of composites (Kaith et al. 2006; Kaith and Kalia 2008).

Mechanical properties of phenolic composites reinforced with graft copolymers of flax fiber and an improvement in mechanical strength of composites has been reported (Kaith and Kalia 2007, 2008). Mechanical properties of polymer-matrix composites reinforced with acrylate grafted henequen cellulose fibers were studied. It was found that best results could be obtained with poly(MMA) grafted cellulose fibers because of

better fiber-matrix adhesion (Canché-Escamilla et al. 1999). The use of graft copolymers of MF is scantily reported in literature. So in the present paper, we have reported the preparation of graft copolymers of MF with vinyl monomers for use in polystyrene composites.

EXPERIMENTAL

Materials

Natural flax fibers (*Linum usitatissimum*) were supplied by the Department of Agronomy, CSK HP Agriculture University, Palampur (India). Flax fibers were Soxhlet extracted with acetone for 72 h. Acrylic acid (AA), acrylonitrile (AN), methyl methacrylate (MMA), vinyl acetate (VA), 4-vinyl pyridine (4-VP), and acrylamide (AAm) (Fluka) were washed with 5% sodium hydroxide followed by water and were dried over anhydrous sodium sulphate. The dried monomers were distilled, and the middle fraction was used. A Libror AEG-220 (Shimadzu make) electronic balance was used for weighing purpose.

IR spectra, SEM, and thermal analysis were carried-out on a Perkin Elmer RXI Spectrophotometer, Electron Microscopy Machine (LEO 435 VP), and thermal analyzer (LINSEIS, L-81 11), respectively.

Mercerization of Flax Fiber

Flax fiber was immersed in 10% NaOH solution for 2-3 minutes at 35°C and then in 1% H₂SO₄ solution. The fiber was immediately taken out and washed with distilled water for removal of acid. However, the final washing was given with slightly alkaline softener in order to neutralize the last traces of acid used. The fiber was kept in an air drier for 15 minutes.

Graft Copolymerization of Vinyl Monomers onto Flax

0.5 gm flax fiber were immersed in 100 ml of distilled water for 24 hrs prior to their grafting. A definite ratio of ferrous ammonium sulphate (FAS) - potassium persulphate (KPS) initiator and a known quantity of vinyl monomers were added to the reaction mixture. The reaction mixture was heated at a particular temperature and stirred constantly. The graft copolymer was Soxhlet extracted with acetone for about 5-6 h so as to remove homopolymer. Further, the traces of homopolymer were separated from graft copolymer by stirring the graft copolymer in acetone for about 24 h using magnetic stirrer. After homopolymer extraction, grafted fiber was dried in an oven at 50°C until a constant weight was obtained, and the percentage graft yield was calculated. Optimization of various reaction parameters was carried-out so as to get maximum graft yield. The percentage of grafting (P_g) was calculated as follows (Kaith and Kalia 2007, 2008):

$$P_g = \frac{W_2 - W_1}{W_1} \times 100, \quad (1)$$

where W_1 and W_2 are the weights of original flax and grafted flax, respectively.

Infra Red Spectroscopy (IR)

IR spectra of the ungrafted and grafted flax fibers were taken with KBr pellets on the Perkin Elmer RXI Spectrophotometer.

Scanning Electron Microscopy (SEM)

Scanning electron microscopic studies of flax and its graft copolymers were carried-out with the Electron Microscopy Machine (LEO 435 VP). Since cellulose has non-conducting behavior, it was gold-sputtered in order to prevent charge buildup on the sample. Scanning was synchronized with the microscopic beam in order to maintain the small size over large distance relative to the specimen. The resulting images had a great depth of the field. A remarkable three-dimensional appearance with high resolution was obtained. The scans could easily verify the fact that cellulosic fibers lying apart in raw sample started forming bundles in the graft copolymers.

Thermo-gravimetric Analysis / Differential Thermal Analysis (TGA/DTA)

Thermogravimetric analysis and differential thermal analysis studies were carried-out in air at a heating rate of 10°C/min on a thermal analyzer (Linseis, L-81 11).

Preparation of Composites

Composites were prepared in a Compression Molding Machine (Santec, India) as per a method reported earlier (Kaith and Kalia 2008). Mechanical studies such as wear-resistance of the composites were carried-out as per ASTM D 3702 on a Wear & Friction Monitor (Ducom, 20LE), and tensile strength and compressive strength of PS composites were carried as per ASTM D 3039 and ASTM D 3410 on Universal Testing Machine (Hounsfield, H25KS), respectively (Kaith and Kalia 2007, 2008). The number of specimens used for the determination of mechanical properties was three and tests were conducted under ambient laboratory conditions.

RESULTS AND DISCUSSION

C₂, C₃, and C₆ hydroxyls and C-H groups are active sites for the incorporation of polymeric chains through grafting onto cellulosic fibers such as flax. In case of graft copolymerization of AA onto MF, optimum reaction conditions for getting maximum graft yield (40.70 %) were : AA = 2.92 x 10⁻³ molL⁻¹, temp. = 45 °C, time = 120 min., and FAS: KPS (molar ratio) = 0.50 : 1.

Grafting of binary vinyl monomer mixtures onto mercerized flax using AA (2.92 x 10⁻³ mol/l) as the principal monomer showed 33.55 % (AN = 1.52 x 10⁻³ mol/l), 21.50 % (VA = 2.17 x 10⁻³ mol/l), 29.73 % (MMA = 2.92 x 10⁻³ mol/l), 4.07 % (4-VP = 2.32 x 10⁻³ mol/l), and 5.10 % (AAm = 1.76 x 10⁻³ mol/l) maximum grafting, respectively (Figs. 1-5). The higher percentage grafting in the case of these binary monomer mixtures can be explained by the fact that the addition of the electron-acceptor monomers AN and MMA, as well as the electron-donor monomer VA, to AA increase the reactivity of AA towards grafting.

A lower percentage of grafting in the case of AA + 4-VP is attributed to the fact

that VP undergoes resonance stabilization, thereby resulting in low free radical sites on the monomeric units, and hence a decreased graft yield has been observed. In case of AA

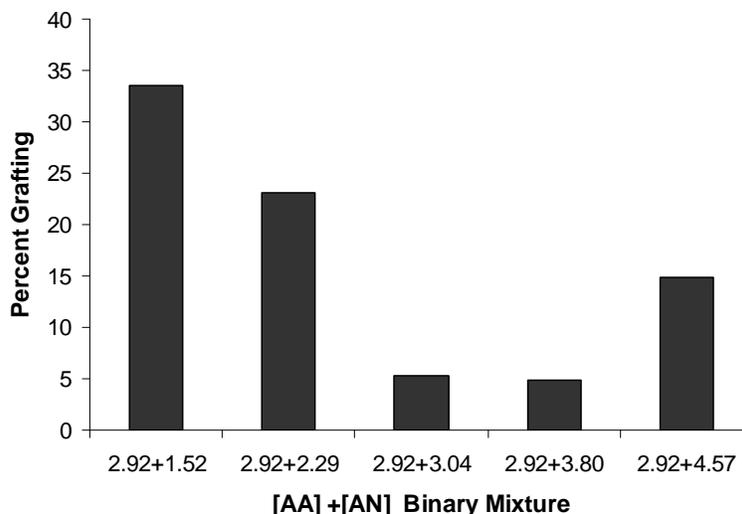


Fig. 1. Effect of AA + AN binary mixture on grafting

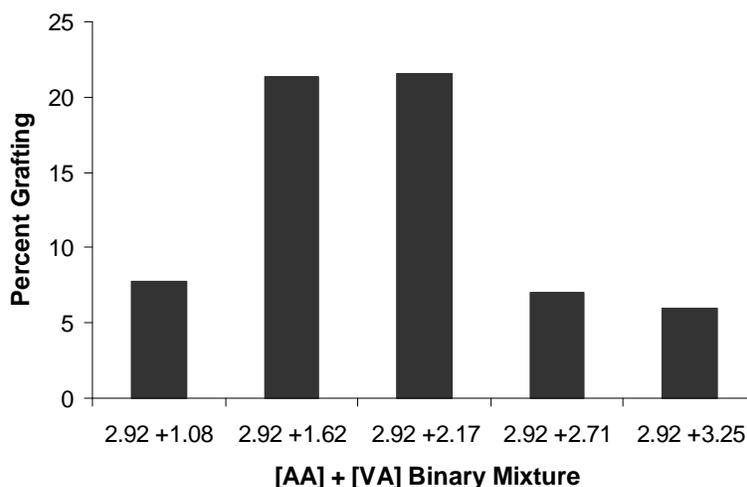


Fig. 2. Effect of AA + VA binary mixture on grafting

+AAm, both are highly soluble in water, which results in formation of less free radical sites on the backbone polymer, and hence a decreased graft yield has been observed.

FT-IR Spectroscopy

Flax fiber showed a broad peak at 3420 cm^{-1} due to bonded $-\text{OH}$, 1747 cm^{-1} due to acetyl group, 2907 cm^{-1} due to C-H stretching, and at 2925 , 1458 , and 1055 cm^{-1} arising from $-\text{CH}_2$, C-C and C-O stretching respectively. On grafting, IR bands due to characteristics functional groups incorporated onto flax have been witnessed apart from the above listed bands.

On the other hand, MF-g-poly(AA+VA), MF-g-poly(AA+AN), MF-g-poly(AA+MMA), MF-g-poly(AA+4-VP), and MF-g-poly(AA+AAm) showed additional peaks at 1711 cm^{-1} and 1731 cm^{-1} due to the carbonyl groups of AA and MMA, respectively and 2670 cm^{-1} due to bonded O-H stretching of AA; 1731 cm^{-1} due to ester group of VA; 2239 cm^{-1} due to nitrile group of AN ; 1440 cm^{-1} due to $-\text{C}=\text{N}$ group of 4-VP ; and 1620 cm^{-1} due to carbonyl group of AAm.

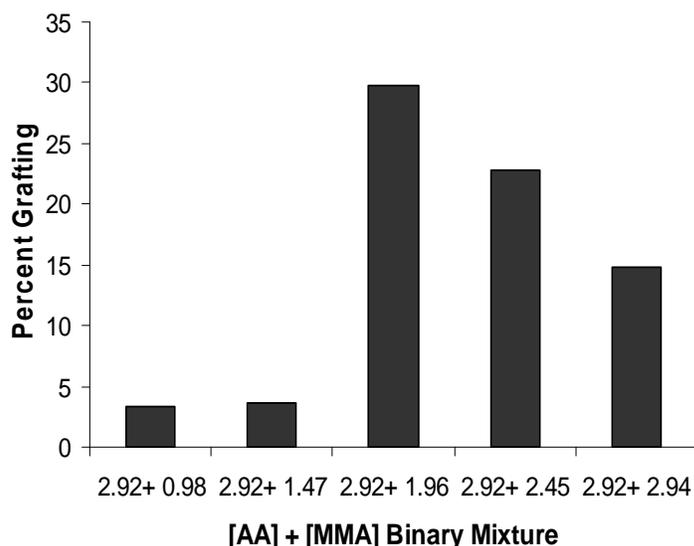


Fig. 3. Effect of AA + MMA binary mixture on grafting

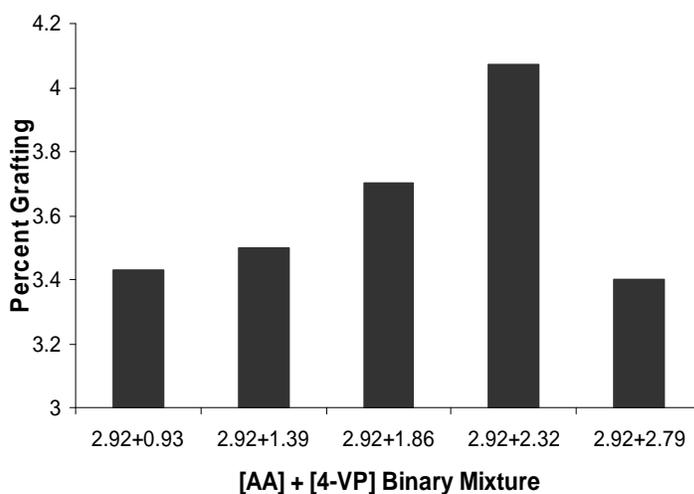


Fig. 4. Effect of AA + 4-VP binary mixture on grafting

Scanning Electron Microscopy (SEM)

A clear-cut distinction between the scanning electron micrographs (SEM) of MF and its graft copolymers was observed (Fig. 6). There was a significant deposition of polymer onto flax fiber. The scans easily verify the fact that cellulosic fibers lying apart in MF started forming bundles in the graft copolymers.

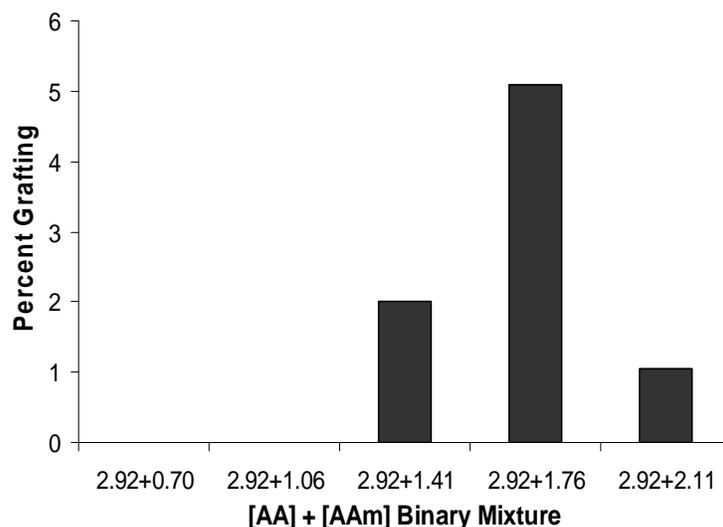


Fig. 5. Effect of AA + AAm binary mixture on grafting

Thermal Behaviour of Graft Copolymers

In the case of MF, two stages of decomposition were found; in the temperature range from 302 to 345 °C the weight loss was 31%, and in the range 345 to 559 °C the weight loss was 39%. The first stage of thermal decomposition showed depolymerization and glucosan formation, and the second stage showed the disturbance in the H-bonded amorphous region and complete break down of C-C and C-O bonds of the crystalline region.

In case of graft copolymers; MF-g-poly(AA+VA), MF-g-poly(AA+AN), MF-g-poly(AA+MMA), MF-g-poly(AA+4-VP), and MF-g-poly(AA+AAm), the initial decomposition temperatures (IDTs) were 38, 310, 42, 322, and 43 °C, respectively, and the final decomposition temperatures (FDTs) were 470, 516, 416, 487, and 453 °C, respectively (Table 1).

Table 1. Thermo-Gravimetric Analysis of Graft Copolymers

Sample	Degradation stages (°C)	Residue (%)	IDT (°C)	FDT (°C)
MF	302-345 345-559	29	307	559
MF-g-poly(AA+AN)	310-355 355-516	29	310	516
MF-g-poly(AA+MMA)	42-304 304-416	0.8	42	416
MF-g-poly(AA+VA)	38-261 261-470	5	38	470
MF-g-poly(AA+4-VP)	322-359 359-487	41	322	487
MF-g-poly(AA+AAm)	43-251 251-453	0	43	453

MF has been found to show higher FDT in comparison to graft copolymers. With the grafting of vinyl monomers, the original crystal lattice of the fibers gets disturbed, which results in the lower final decomposition temperature of the graft copolymers. Thus it has been observed that there exists a direct correlation between percentage of grafting and crystallinity.

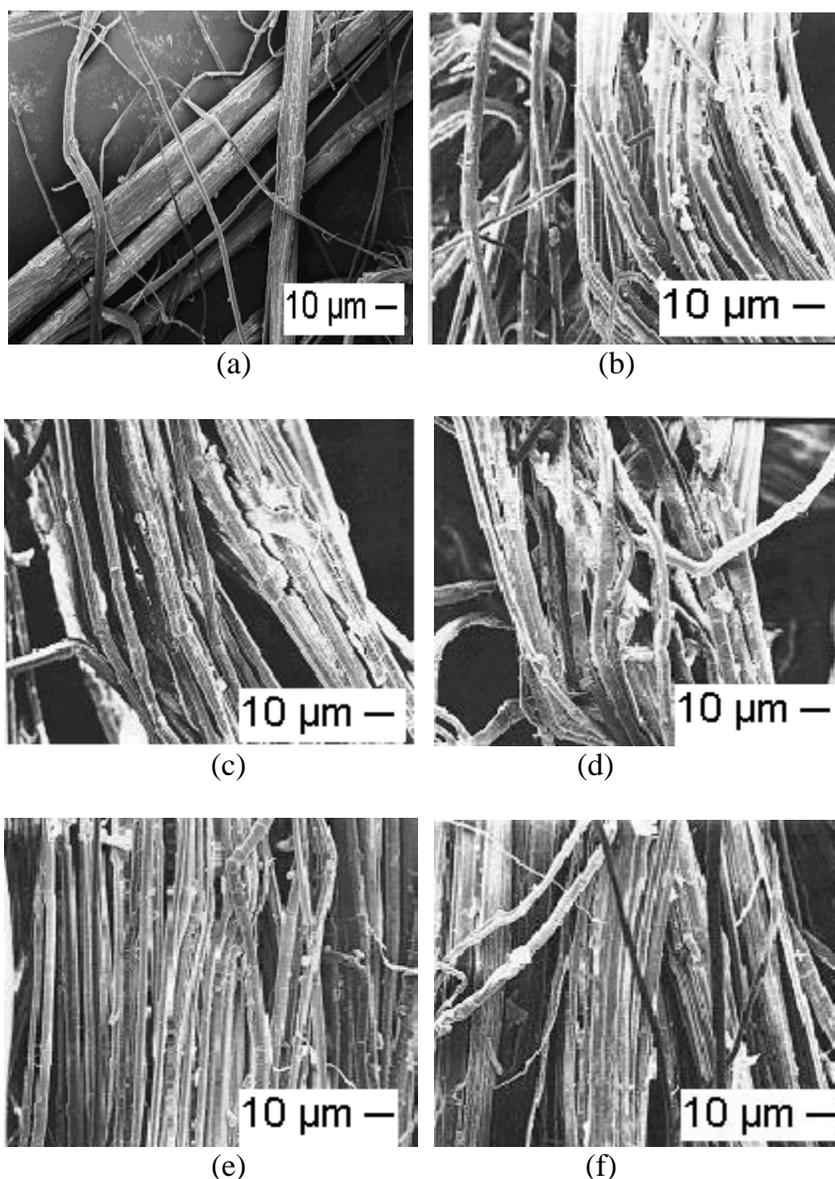


Fig. 6. Scanning electron micrographs: (a) MF, (b) MF-g-poly(AA+AN), (c) MF-g-poly(AA+VA), (d) MF-poly(AA+MMA), (e) MF-g-poly(AA+4-VP), (f) MF-g-poly(AA+AAM).

Wear Resistance

It is evident from Table 2 that polystyrene (PS) matrix showed 6.21, 7.91, 8.86, 10.33, and 16.76 gm/m x 10⁻⁶ wear rate. MF-reinforced PS composites showed 0.708, 1.12, 1.54, 2.4, and 6.15 gm/m x 10⁻⁶ wear rate, at 0.2 0.5, 1.0, 1.5, and 2 Kg loads, respectively. It has been observed that composites reinforced with MF-g-

poly(AA+MMA); MF-g-poly(AA+4-VP); MF-g-poly(AA+AAM); Flax-g-MF-g-poly(AA+VA); and MF-g-poly(AA+AN) showed 1.69, 3.41, 4.76, 6.96, and 7.98 gm/m x 10⁻⁶; 1.54, 2.48, 4.79, 5.32, and 6.10 gm/m x 10⁻⁶; 2.72, 4.15, 5.92, 6.12, and 7.23 gm/m x 10⁻⁶; 2.13, 4.04, 5.29, 6.14, and 7.03 gm/m x 10⁻⁶; 1.19, 3.35, 4.03, 4.92, and 5.92 gm/m x 10⁻⁶; and 1.1, 2.13, 3.43, 4.09, and 5.19 gm/m x 10⁻⁴ wear rate at 0.2 0.5, 1, 1.5, and 2 Kg loads, respectively.

Table 2. Mechanical Properties of Mercerized Flax and Graft Copolymers Reinforced PS Composites

Sample	Tensile Strength (N)	Compressive Strength (N)	Wear Rate (gm/m) x 10 ⁻⁴				
			0.2 Kg	0.5 Kg	1 Kg	1.5 Kg	2 Kg
PS Matrix	125	100	6.21	7.91	8.86	10.33	10.76
MF Reinforced PS Composites	175	500	0.708	1.12	1.54	2.4	6.15
MF-g-poly(AA+AN) Reinforced PS Composites	175	300	1.10	2.13	3.43	4.09	5.19
MF-g-poly(AA+MMA) Reinforced PS Composites	150	400	1.69	3.41	4.76	6.96	7.98
MF-g-poly(AA+VA) Reinforced PS Composites	175	530	2.13	4.04	5.29	6.14	7.03
MF-g-poly(AA+4-VP) Reinforced PS Composites	150	615	1.54	2.48	4.79	5.32	6.10
MF-g-poly(AA+AAM) Reinforced PS Composites	175	500	2.72	4.15	5.92	6.12	7.23

Compressive Strength

In case of reinforcement with MF, composites could bear a load of 500 Newtons force with compression of 1.3 mm, respectively. Pure polystyrene could withstand up to a load of 100 Newtons force with a compression of 0.27 mm.

Composites reinforced with MF-g-poly(AA+AAM) achieved success up to the load of 500 Newtons force with compression of 1.2 mm, whereas in the case of reinforcement with MF-g-poly(AA+MMA) success was achieved up to a load of 400 Newtons force with compression of 2.6 mm. In case of reinforcement with MF-g-poly(AA+AN), composites broke at a load of 300 Newtons force with compression of 2.6 mm. PS composites reinforced with MF-g-poly(AA+4-VP) and MF-g-poly(AA+VA)

could bear a load of 615 and 530 Newtons force with compression of 0.73 and 1.24 mm, respectively (Table 2).

Tensile Strength

A composite reinforced with MF fibers was successful only up to 175 Newtons force with extension of 4.7 mm. Pure polystyrene matrix could not withstand up to the load of 125 Newtons force with an extension of 0.42 mm.

In the case of reinforcement with MF-g-poly(AA+MMA) and MF-g-poly(AA+4-VP), composites could not bear the load of 150 Newtons force with extension of 2.9 and 3.1 mm, respectively, but composites reinforced with MF-g-poly(AA+AAM), MF-g-poly(AA+VA), and MF-g-poly(AA+AN) achieved success up to a load of 175 Newtons force with extension of 4.5, 0.65, and 0.62 mm respectively (Table 2).

PS composites reinforced with graft copolymers showed enhanced mechanical properties because grafting increased the hydrophobicity of flax fibers and improved the interface between PS matrix and fibers (Canche-Escamilla et al. 1999; Kaith and Kalia 2008). Composites reinforced with mercerized flax also showed improved mechanical strength in comparison to a pure polystyrene matrix, as mercerization improves the hydrophobicity of flax fibers.

CONCLUSIONS

1. A binary vinyl monomer mixture of AA+AN has been found to show maximum grafting onto mercerized flax.
2. Mercerized flax has been found to show better thermal stability in comparison to graft copolymers.
3. In comparison to pure polystyrene matrix, composites reinforced with mercerized flax and graft copolymers showed enhanced mechanical properties.

REFERENCES CITED

- Canche-Escamilla, G., Cauch-Cupul, J. I., Mendizábal, E., Puig, J. E., Vázquez-Torres, H., and Herrera-Franco, P. J. (1999). "Mechanical properties of acrylate-grafted henequen cellulose fibers and their application in composites," *Composites: Part A* 30, 349-359.
- Kaith, B. S., Singha, A. S., and Kumar, S. (2005). "FAS-H₂O₂ initiated graft copolymerization of methylmethacrylate onto flax and evaluation of some physical and chemical properties," *J. Polym. Mater.* 22, 425-432.
- Kaith, B. S., and Kalia, S. (2007). "Synthesis and characterization of graft copolymers of flax with binary vinyl monomers," *Int. J. Polym. Anal. Charact.* 12, 401-412.
- Kaith, B. S., and Kalia, S. (2007). "Grafting of flax fiber (*Linum usitatissimum*) with vinyl monomers for enhancement of properties of flax-phenolic composites," *Polym. J.* 39, 1319-1327.

- Kaith, B. S., Singha, A. S., and Kalia, S. (2007). "Grafting of MMA onto flax under the influence of microwave radiations and use of flax-g-poly(MMA) in the preparation of PF composites," *Autex Res. J.* 7, 119-129.
- Kaith, B. S., and Kalia, S. (2008). "Evaluation of crystallinity of graft copolymers of flax with binary vinyl monomers," *e-Polymers no.* 002.
- Kaith, B. S., and Kalia, S. (2008). "Graft copolymerization of MMA onto flax under different reaction conditions: A comparative study," *Express Polym. Lett.* 2, 93-100.
- Kaith, B. S., and Kalia, S. (2008). "Mechanical properties of flax-g-poly(methyl acrylate) reinforced phenolic composites," *Fibers and Polymers* (in press).
- Kaith, B. S., and Kalia, S. (2008). "Preparation of microwave radiation induced graft copolymers and their applications as reinforcing material in phenolic composites," *Polym. Compos.* 29, 791-797.
- Kalia, S., and Kaith, B. S. (2008). "Microwave enhanced synthesis of Flax-g-poly(MMA) for use in phenolic composites as reinforcement," *E. J. Chem.* 5, 163-168.
- Karmaker, A. C. (1997), "Effect of water absorption on dimensional stability and impact energy of jute fibre reinforced polypropylene," *J. Mat. Sci. Lett.* 16, 462-464.
- Katz, H. S., and Milewski, J. V. (eds.) (1987). *Handbook of Fillers for Plastics*, Van Nostrand Reinhold, Section VI, New York.
- Nada, A. M. A., Alkady, M. Y., and Fekri, H. M. (2007). "Synthesis and characterization of grafted cellulose for use in water and metal ions sorption," *Bioresources* 3, 46-59.

Article submitted: June 18, 2008; Peer-review completed: July 25, 2008; Revision received and accepted: August 8, 2008; Published Aug 9, 2008.